

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE  
REQUEST FOR FILING NATIONAL PHASE OF  
PCT APPLICATION UNDER 35 U.S.C. 371 AND 37 CFR 1.494 OR 1.495

09/857303

To: Hon. Commissioner of Patents  
Washington, D.C. 20231



00909

TRANSMITTAL LETTER TO THE UNITED STATES  
DESIGNATED/ELIGIBLE OFFICE (DO/EO/US)

Atty Dkt: P 0280366 /B99/1785QT  
M# /Client Ref.

From: Pillsbury Winthrop LLP, IP Group:

Date: June 1, 2001

This is a **REQUEST** for **FILING** a PCT/USA National Phase Application based on:

1. International Application <u>PCT/FR00/02687</u> ↑ country code	2. International Filing Date <u>28 September 2000</u> Day MONTH Year	3. Earliest Priority Date Claimed <u>1 October 1999</u> Day MONTH Year (use item 2 if no earlier priority)
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4. Measured from the earliest priority date in item 3, this PCT/USA National Phase Application Request is being filed within:

(a) ☒ 20 months from above item 3 date (b) ☐ 30 months from above item 3 date,

(c) Therefore, the due date (unextendable) is June 1, 2001

Title of Invention MATERIAL COMPRISING AN ORGANIC UV-A FILTER AND METHOD FOR DISPLACING THE MAXIMUM ABSORPTION WAVELENGTH

Inventor(s) Sandrine Chodorowski, Francis Xavier Quinn and Clement Sanchez

Applicant herewith submits the following under 35 U.S.C. 371 to effect filing:

☒ Please immediately start national examination procedures (35 U.S.C. 371 (f)).

☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2)) is transmitted herewith (file if in English but, if in foreign language, file only if not transmitted to PTO by the International Bureau) including:

- a. ☒ Request;
- b. ☒ Abstract;
- c. 38 pgs. Spec. and Claims;
- d.    sheet(s) Drawing which are ☐ informal ☐ formal of size ☐ A4 ☐ 11"

9. ☒ A copy of the International Application has been transmitted by the International Bureau.

10. A translation of the International Application into English (35 U.S.C. 371(c)(2))

- a. ☒ is transmitted herewith including: (1) ☐ Request; (2) ☒ Abstract;  
(3) 38 pgs. Spec. and Claims;  
(4)    sheet(s) Drawing which are:  
☐ informal ☐ formal of size ☐ A4 ☐ 11"
- b. ☐ is not required, as the application was filed in English.
- c. ☐ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.
- d. ☐ Translation verification attached (not required now).

JC05 Rec'd PCT/PTO 01 JUN 2001

11. ☒ Please see the attached Preliminary Amendment
12. ☐ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., **before 18th month from first priority date above in item 3, are transmitted herewith (file only if in English) including:**
13. ☒ PCT Article 19 claim amendments (if any) have been transmitted by the International Bureau
14. ☐ Translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)), i.e., of **claim amendments** made before 18th month, **is attached (required by 20th month from the date in item 3 if box 4(a) above is X'd, or 30th month if box 4(b) is X'd, or else amendments will be considered canceled).**

15. **A declaration of the inventor** (35 U.S.C. 371(c)(4))

- a. ☐ is submitted herewith ☐ Original ☐ Facsimile/Copy
- b. ☒ is not herewith, but will be filed when required by the forthcoming PTO Missing Requirements Notice per Rule 494(c) if box 4(a) is X'd or Rule 495(c) if box 4(b) is X'd.

16. **An International Search Report (ISR):**

- a. Was prepared by ☐ European Patent Office ☐ Japanese Patent Office ☐ Other
- b. ☐ has been transmitted by the international Bureau to PTO.
- c. ☐ copy herewith (\_\_\_ pg(s).) ☐ plus Annex of family members (\_\_\_ pg(s).).

**International Preliminary Examination Report (IPER):**

- a. ☐ has been transmitted (if this letter is filed after 28 months from date in item 3) in English by the International Bureau with Annexes (if any) in original language.
- b. ☐ copy herewith in English.
- c.1 ☐ IPER Annex(es) in original language ("Annexes" are amendments made to claims/spec/drawings during Examination) including attached amended:
- c.2 ☐ Specification/claim pages #\_\_\_ claims #  
Dwg Sheets #
- d. ☐ Translation of Annex(es) to IPER **(required by 30<sup>th</sup> month due date, or else annexed amendments will be considered canceled).**

**Information Disclosure Statement** including:

- a. ☐ Attached Form PTO-1449 listing documents
- b. ☐ Attached copies of documents listed on Form PTO-1449
- c. ☐ A concise explanation of relevance of ISR references is given in the ISR.

19. ☐ **Assignment** document and Cover Sheet for recording are attached. Please mail the recorded assignment document back to the person whose signature, name and address appear at the end of this letter.
20. ☐ Copy of Power to IA agent.
21. ☐ **Drawings** (complete only if 8d or 10a(4) not completed): \_\_\_ sheet(s) per set: ☐ 1 set informal; ☐ Formal of size ☐ A4 ☐ 11"

22. Small Entity Status ☒ is **Not** claimed ☐ is claimed (pre-filing confirmation required)
- 22(a) \_\_\_ (No.) Small Entity Statement(s) enclosed (since 9/8/00 Small Entity Statements(s) not essential to make claim)

23. **Priority** is hereby claimed under 35 U.S.C. 119/365 based on the priority claim and the certified copy, both filed in the International Application during the international stage based on the filing in (country) France of:

	<u>Application No.</u>	<u>Filing Date</u>		<u>Application No.</u>	<u>Filing Date</u>
(1)	99/12321	1 October 1999	(2)	_____	_____
(3)	_____	_____	(4)	_____	_____
(5)	_____	_____	(6)	_____	_____

- a. ☒ See Form PCT/IB/304 sent to US/DO with copy of priority documents. If copy has not been received, please proceed promptly to obtain same from the IB.
- b. ☐ Copy of Form PCT/IB/304 attached.

RE: USA National Phase Filing of PCT/FR00/02687

JC05 Rec'd PCT/PTO

01 JUN 2007

24. Attached: Preliminary Amendment

25 Per Item 17.c2, **cancel original** pages #\_\_, claims #\_\_, Drawing Sheets #26. **Calculation of the U.S. National Fee (35 U.S.C. 371 (c)(1)) and other fees is as follows:**Based on amended claim(s) per above item(s) ☐ 12, ☐ 14, ☐ 17, ☐ 25 (hilitte)

Total Effective Claims	60	minus 20 =	40	x \$18/\$9	=	\$720	966/967
Independent Claims	2	minus 3 =	0	x \$80/\$40	=	\$0	964/965
If any proper (ignore improper) Multiple Dependent claim is present,				add \$270/\$135	+	0	968/969

BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(4)): →→ **BASIC FEE REQUIRED, NOW** →→→→A. If country code letters in item 1 are not "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"

See item 16 re:

1. Search Report was <u>not</u> prepared by EPO or JPO -----	add \$1000/\$500	960/961
2. Search Report was prepared by EPO or JPO -----	add \$860/\$430 +1000	970/971

**SKIP B, C, D AND E UNLESS country code letters in item 1 are "US", "BR", "BB", "TT", "MX", "IL", "NZ", "IN" or "ZA"**

→ <input type="checkbox"/> B. If <u>USPTO</u> did not issue <u>both</u> International Search Report (ISR) and (if box 4(b) above is X'd) the International Examination Report (IPER), -----	add \$1000/\$500	+0	960/961
→ <input type="checkbox"/> C. If <u>USPTO</u> issued ISR but not IPER (or box 4(a) above is X'd), -----	add \$710/\$355	+0	958/959
→ <input type="checkbox"/> D. If <u>USPTO</u> issued IPER but IPER Sec. V boxes <u>not all</u> 3 YES, -----	add \$690/\$345	+0	956/957
→ <input type="checkbox"/> E. If international preliminary examination fee was paid to <u>USPTO</u> and Rules 492(a)(4) and 496(b) <u>satisfied</u> (IPER Sec. V <u>all</u> 3 boxes YES for <u>all</u> claims), -----	add \$100/\$50	+0	962/963
<b>SUBTOTAL =</b>		<b>\$1720</b>	

28. If Assignment box 19 above is X'd, add Assignment Recording fee of ----\$40 +0 (581)

29. CHARGE the requisite fees to Deposit Account- ----- **TOTAL FEES** **\$1720**

CHARGE Deposit Account No. 03-3975

Our Order No. 012237 0280366  
C# M#

00909

**CHARGE STATEMENT:** The Commissioner is hereby authorized to charge any fee specifically authorized hereafter, or any missing or insufficient fee(s) filed, or asserted to be filed, or which should have been filed herewith or concerning any paper filed hereafter, and which may be required under Rules 16-18 and 492 (missing or insufficient fee only) now or hereafter relative to this application and the resulting Official document under Rule 20, or credit any overpayment, to our Account/Order Nos. shown above for which purpose a duplicate copy of this sheet is attached.**This CHARGE STATEMENT does not authorize charge of the issue fee until/unless an issue fee transmittal form is filed****Pillsbury Winthrop LLP**  
**Intellectual Property Group**By Atty: Samir ElamraniReg. No. 43,601

Sig:

Fax: (202) 822-0944  
Tel: (202) 861-3664

Atty/Sec: SE/kmh

**NOTE:** File in duplicate with 2 postcard receipts (PAT-103) & attachments.

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re PATENT APPLICATION OF

BOX PCT

Sandrine Chodorowski et al.

Group Art Unit: Unassigned

Application No. (corresponds to PCT/FR00/02687)

Examiner: Unassigned

Filed: June 1, 2001

Title: MATERIAL COMPRISING AN ORGANIC UV-A FILTER AND METHOD FOR DISPLACING THE  
MAXIMUM ABSORPTION WAVELENGTH

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Prior to examination of the above-identified application, please amend the application  
as follows.

**In the Claims**

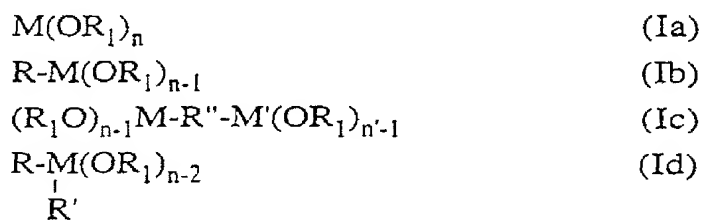
Please cancel Claims 1-38 without prejudice or disclaimer and enter the following  
new Claims 39-97:

--39. A material comprising:

- (a) at least one metal alkoxide selected from the group consisting of zirconium, titanium and aluminum alkoxides;
  - (b) at least one organic UV-A sunscreen agent having a maximum absorption wavelength of less than 370 nm;
  - (c) at least one functionalized organic polymer or a precursor thereof, or at least one functionalized silicone polymer or a precursor thereof;
  - (d) at least one solvent, and
  - (e) an amount of water sufficient for at least partial hydrolysis of the metal alkoxide and its condensation; and
- wherein said material has a maximum absorption wavelength ( $\lambda_{\max}$ ) of from 370 to 400 nm.

40. The material of Claim 39 prepared by the sol-gel route.

41. The material of Claim 39, wherein the amount of water is sufficient for complete hydrolysis of the metal alkoxide.
42. The material according to Claim 39, wherein the metal alkoxide is selected from the group consisting of:
- (1) metalloorganic compounds corresponding to one of the following formulae:



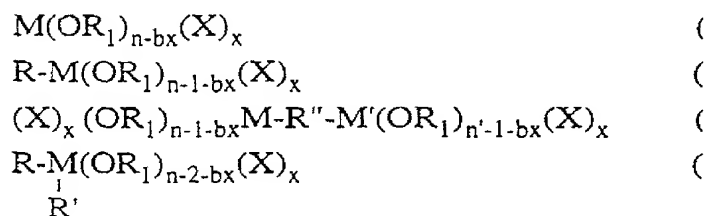
wherein M and M' represent, independently of one another, a zirconium, titanium or aluminum atom, n and n' denote the respective valencies of the metal atoms represented by M and M',

R<sub>1</sub> represents a saturated or unsaturated, linear or branched C<sub>1-30</sub> hydrocarbonaceous group,

R and R' represent, independently of one another, a saturated or unsaturated, linear, branched or cyclic C<sub>1-30</sub> hydrocarbonaceous group,

R'' represents a saturated or unsaturated, linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group; and

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



wherein: M, M', n, n', R<sub>1</sub>, R, R' and R'' are as defined above;

X represents a monodentate or polydentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic

polymer or said functionalized silicone polymer (c), x represents the number of X ligands; and

b represents the number of bonding atoms of the X ligand.

43. The material of Claim 42, wherein  $R_1$  represents a saturated or unsaturated, linear or branched  $C_{1-6}$  hydrocarbonaceous group.
44. The material of Claim 42, wherein  $R_1$  represents a saturated or unsaturated, linear or branched hydrocarbonaceous group comprising a heteroatom.
45. The material of Claim 44, wherein the heteroatom is selected from the group consisting of nitrogen, sulfur, oxygen and phosphorus.
46. The material of Claim 42, wherein R and  $R'$  are independently  $C_{2-20}$  hydrocarbonaceous group.
47. The material of Claim 42, wherein R and  $R'$ , independently comprise a heteroatom selected from the group consisting of nitrogen, phosphorus, sulfur and oxygen.
48. The material of Claim 42, wherein R and  $R'$ , are independently selected from the group consisting of linear and branched alkyls, cycloalkyls and aryls.
49. The material of Claim 42, wherein R and  $R'$  are independently substituted by groups capable of reacting with the organic or silicone polymer.
50. The material of Claim 42, wherein R and  $R'$  independently comprise a cosmetically or dermatologically active group.
51. The material of Claim 42, wherein  $R''$  comprises a heteroatom selected from the group consisting of nitrogen, phosphorus, sulfur and oxygen.
52. The material of Claim 42, wherein  $R''$  is selected from the group consisting of linear and branched, cycloalkylenes, and arylene.

53. The material of Claim 42, wherein R'' is substituted by a group capable of reacting with the organic or silicone polymer.
54. The material of Claim 42, wherein R'' comprises a cosmetically or dermatologically active group.
55. The material of Claim 42, wherein X comprises a cosmetically or dermatologically active group.
56. The material according to Claim 42, wherein at least one of R, R', R'' and/ X comprises a group capable of reacting with the functionalized organic polymer or the functionalized silicone polymer (c) selected from the group consisting of halogen atoms, hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino, pyrrolo, a group comprising ethylenic unsaturation selected from the group consisting of (meth)acrylic and vinyl groups, halogenated groups, hydroxylated and carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives.
57. The material of Claim 42, wherein the monodentate or polydentate ligand X is selected from the group consisting of sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers), monoalcohols and polyols, dextrin and its derivatives, and thiazolidines.
58. The material of Claim 57, wherein the monodentate or polydentate ligand X is selected from the group consisting of  $\alpha$ - and  $\beta$ -hydroxylated amino acids, and derivatives thereof.
59. The material of Claim 39 wherein the metal alkoxide is selected from the group consisting of tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

60. The material of Claim 39, wherein the metal alkoxide is present in an amount ranging from 0.1% by weight to 99% by weight, with respect to the total weight of the material.
61. The material of Claim 39, wherein the metal alkoxide is present in an amount ranging from 0.5% by weight to 80% by weight, with respect to the total weight of the material.
62. The material of Claim 39, wherein the organic UV-A sunscreen agent is selected from the group consisting of:
- dibenzoylmethane derivatives,
  - camphor derivatives,
  - benzimidazole derivatives,
  - benzoxazole derivatives,
  - benzophenone derivatives,
  - silane or polyorganosiloxane derivatives comprising benzophenone group(s),
  - anthranilates, and
  - their mixtures.
63. The material of Claim 39, wherein the organic UV-A sunscreen agent is selected from the group consisting of:
- 2-methyldibenzoylmethane,
  - 4-methyldibenzoylmethane,
  - 4-isopropyldibenzoylmethane,
  - 4-tert-butyldibenzoylmethane,
  - 2,4-dimethyldibenzoylmethane,
  - 2,5-dimethyldibenzoylmethane,
  - 4,4'-diisopropyldibenzoylmethane,
  - 4,4'-dimethoxydibenzoylmethane,
  - 4-tert-butyl-4'-methoxydibenzoylmethane,
  - 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
  - 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,
  - 2,4-dimethyl-4'-methoxydibenzoylmethane, and
  - 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.



64. The material of Claim 39, wherein the organic UV-A sunscreen agent is 4-tert-butyl-4'-methoxydibenzoylmethane.
65. The material of Claim 39, wherein the organic UV-A sunscreen agent is present in an amount ranging from 0.1% by weight to 60% by weight, with respect to the total weight of the material.
66. The material of Claim 39, wherein the organic UV-A sunscreen agent is present in an amount ranging from 0.1% to 30% by weight, with respect to the total weight of the material.
67. The material of Claim 39, wherein the functionalized organic or silicone polymer is a homopolymer or random, block and/or graft copolymer selected from the group consisting of:
- (a) alkyloxazoline homopolymers and copolymers;
  - (b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;
  - (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
  - (d) vinyl alcohol homopolymers and copolymers;
  - (e) homopolymers of vinyl and/or allyl and/or methallyl esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
  - (f) polyethers;
  - (g) polyesters;
  - (h) homopolymers and copolymers of olefins or of cycloolefins;

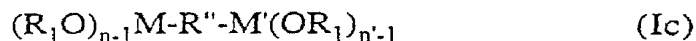
- (i) polyamides and polyesteramides;
- (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers;
- (l) natural polymers and modified natural polymers;
- (m) polyorganosiloxanes;
- (n) polyorganophosphazenes;
- (o) polysilanes, polycarbosilanes or polysilazanes; and
- (p) mixtures of these polymers.

68. The material of Claim 39, wherein the functionalized organic or silicone polymer is selected from the group consisting of poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(aryl alcohol) and poly(vinylpyrrolidone).
69. The material of Claim 68, wherein the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.
70. The material of Claim 39, wherein the functionalized organic or silicone polymer is present in an amount ranging from 0.1% by weight to 99% by weight, with respect to the total weight of the material.
71. The material of Claim 39, wherein the functionalized organic or silicone polymer is present in an amount ranging from 0.5% to 80% by weight, with respect to the total weight of the material.
72. The material of Claim 39, wherein the solvent is an alcohol.
73. The material of Claim 72, wherein the alcohol is a linear or branched lower alcohol.
74. The material of Claim 73, wherein the alcohol is ethanol.
75. A cosmetic and/or dermatological composition comprising an effective amount of the material of Claim 39 in a cosmetically and/or dermatologically acceptable vehicle.

76. The cosmetic and/or dermatological composition of Claim 75, wherein the material is in the form of particles obtained by drying and milling.
77. The cosmetic and/or dermatological composition of Claim 75, wherein the material is present in an amount from 1% by weight to 99% by weight with respect to the total weight of the cosmetic and/or dermatological composition.
78. The cosmetic and/or dermatological composition of Claim 75, wherein the material is present in an amount from 5% by weight to 60% by weight with respect to the total weight of the cosmetic and/or dermatological composition.
79. The cosmetic and/or dermatological composition of Claim 75, wherein the mean size of particles obtained by drying and milling the material is from 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ .
80. The cosmetic and/or dermatological composition of Claim 75, wherein the mean size of particles obtained by drying and milling the material is from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ .
81. The cosmetic and/or dermatological composition of Claim 75, further comprising an additive selected from the group consisting of sunscreen agents other than organic UV-A sunscreen agents, agents for the artificial tanning and/or browning of the skin, pigments, fatty substances, organic solvents, thickeners, softeners and antioxidants.
82. A process for shifting the maximum absorption wavelength ( $\lambda_{\text{max}}$ ) of an organic UV-A sunscreen agent having a  $\lambda_{\text{max}}$  of less than 370 nm into the range from 370 to 400 nm, wherein the process comprises combining the sun screening agent with a sol comprising at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one solvent and an amount of water sufficient for at least the partial hydrolysis of the metal alkoxide and its condensation.
83. The process of Claim 82, wherein the amount of water is sufficient for complete hydrolysis of the metal alkoxide.

84. The process according to Claim 82, wherein the metal alkoxide is selected from the group consisting of:

(1) metalloorganic compounds corresponding to one of the following formulae:



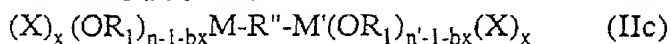
wherein M and M' represent, independently of one another, a zirconium, titanium or aluminum atom, n and n' denote the respective valencies of the metal atoms represented by M and M',

R<sub>1</sub> represents a saturated or unsaturated, linear or branched C<sub>1-30</sub> hydrocarbonaceous group,

R and R' represent, independently of one another, a saturated or unsaturated, linear, branched or cyclic C<sub>1-30</sub> hydrocarbonaceous group optionally

R'' represents a saturated or unsaturated, linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group; and

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



wherein: M, M', n, n', R<sub>1</sub>, R, R' and R'' are as defined above;

X represents a monodentate or polydentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), x represents the number of X ligands; and b represents the number of bonding atoms of the X ligand.

85. The process of Claim 42, wherein  $R_1$  represents a saturated or unsaturated, linear or branched  $C_{1-6}$  hydrocarbonaceous group.
86. The process according to Claim 84, wherein at least one of R, R', R'' and/ X comprises a group capable of reacting with the functionalized organic polymer or the functionalized silicone polymer (c) selected from the group consisting of halogen atoms, hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino, pyrrolo, a group comprising ethylenic unsaturation selected from the group consisting of (meth)acrylic and vinyl groups, halogenated groups, hydroxylated and carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives.
87. The process of Claim 84, wherein the monodentate or polydentate ligand X is selected from the group consisting of sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers), monoalcohols and polyols, dextrin and its derivatives, and thiazolidines.
88. The process of Claim 84, wherein the monodentate or polydentate ligand X is selected from the group consisting of  $\alpha$ - and  $\beta$ -hydroxylated amino acids, and derivatives thereof.
89. The process of Claim 82 wherein the metal alkoxide is selected from the group consisting of tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.
90. The process of Claim 82, wherein the organic UV-A sunscreen agent is selected from the group consisting of:
- dibenzoylmethane derivatives,
  - camphor derivatives,

- benzimidazole derivatives,
- benzoxazole derivatives,
- benzophenone derivatives,
- silane or polyorganosiloxane derivatives comprising benzophenone group(s),
- anthranilates, and
- their mixtures.

90. The process of Claim 82, wherein the organic UV-A sunscreen agent is selected from the group consisting of:

- 2-methyldibenzoylmethane,
- 4-methyldibenzoylmethane,
- 4-isopropyldibenzoylmethane,
- 4-tert-butyldibenzoylmethane,
- 2,4-dimethyldibenzoylmethane,
- 2,5-dimethyldibenzoylmethane,
- 4,4'-diisopropyldibenzoylmethane,
- 4,4'-dimethoxydibenzoylmethane,
- 4-tert-butyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,
- 2,4-dimethyl-4'-methoxydibenzoylmethane, and
- 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

91. The process of Claim 82, wherein the organic UV-A sunscreen agent is 4-tert-butyl-4'-methoxydibenzoylmethane.

92. The process of Claim 82, wherein the functionalized organic or silicone polymer is a homopolymer or random, block and/or graft copolymer selected from the group consisting of:

- (a) alkyloxazoline homopolymers and copolymers;
- (b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids,

phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;

- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (f) polyethers;
- (g) polyesters;
- (h) homopolymers and copolymers of olefins or of cycloolefins;
- (i) polyamides and polyesteramides;
- (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers;
- (l) natural polymers and modified natural polymers;
- (m) polyorganosiloxanes;
- (n) polyorganophosphazenes;
- (o) polysilanes, polycarbosilanes or polysilazanes; and
- (q) mixtures of these polymers.

93. The process of Claim 82, wherein the functionalized organic or silicone polymer is selected from the group consisting of poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(amy alcohol) and poly(vinylpyrrolidone).
94. The process of Claim 82, wherein the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.
95. The process of Claim 82, wherein the solvent is an alcohol.

96. The material of Claim 95, wherein the alcohol is a linear or branched lower alcohol.
97. The process of Claim 96, wherein the alcohol is ethanol.--

**Remarks**

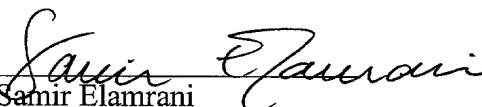
By the above amendments, Claims 1-38 have been rewritten as new Claims 39-97 in conformity with U.S. practice. In particular, the claims have been revised to remove multiple dependencies and non-conventional terminology. No new matter has been introduced by the subject amendments.

In view of the foregoing, the claims are now believed to be in form for allowance, and such action is hereby solicited. If any points remain in issue which the Examiner feels may be best resolved through a personal or telephone interview, he is kindly requested to contact the undersigned at the telephone number listed below.

It is respectfully submitted that the present application is in a condition for allowance and a Notice to that effect is earnestly solicited.

Respectfully submitted,

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Date: June 1, 2001



**MATERIAL COMPRISING AN ORGANIC UV-A SCREENING AGENT AND  
PROCESS FOR SHIFTING THE MAXIMUM ABSORPTION WAVELENGTH**

The present invention generally relates to a  
5 material obtained by the sol-gel route exhibiting a  
maximum absorption wavelength ( $\lambda_{\max}$ ) within the range from  
370 to 400 nm, to a process for shifting the maximum  
absorption wavelength of a material comprising an organic  
UV-A sunscreen agent and to a cosmetic and/or  
10 dermatological composition including such a material.

It is known that light radiation with wavelengths  
of between 280 nm and 400 nm makes possible browning of  
the human epidermis and that rays with wavelengths of  
between 280 nm and 320 nm, known under the name of UV-B  
15 radiation, result in erythemas and cutaneous burns which  
can be harmful to the development of natural tanning;  
this UV-B radiation therefore has to be screened out.

It is also known that UV-A rays with wavelengths  
of between 320 and 400 nm, which result in browning of  
20 the skin, are capable of bringing about a detrimental  
change in the latter, in particular in the case of  
sensitive skin or of skin continually exposed to solar  
radiation. UV-A rays result in particular in a loss of  
elasticity of the skin and the appearance of wrinkles,  
25 leading to premature aging. They promote the triggering  
of the erythematous reaction or enhance this reaction in  
some subjects and can even be the cause of phototoxic or  
photoallergic reactions. It is therefore desirable also  
to screen out UV-A radiation.

30 The commonly used sunscreen agents do not include  
organic screening agents effective in the long UV-A  
spectral range corresponding to wavelengths ranging from  
370 to 400 nm. In other words, antisun protection is not  
provided in this spectral range. This is all the more  
35 serious as this more penetrating radiation is partly  
responsible for the development of certain skin cancers

and of immunosuppression, in addition to cutaneous photoaging.

In the state of the prior art, Patent Applications PCT numbers WO 93/10753 and WO 93/11135 of Slavtcheff et al. respectively disclose a sunscreen agent of metal complex of dibenzoylmethane derivatives type, the maximum absorption wavelength of which is 366 nm, and a process for the preparation of this novel sunscreen agent. Currently, appropriate organic UV-A sunscreen agents exhibiting a maximum absorption wavelength ( $\lambda_{\max}$ ) of greater than or equal to 370 nm with a coefficient of extinction  $\epsilon > 25\ 000\ \text{mol}^{-1}.\text{l}^{-1}.\text{cm}^{-1}$ , preferably  $\epsilon > 30\ 000\ \text{mol}^{-1}.\text{l}^{-1}.\text{cm}^{-1}$ , are unknown.

It has been found, surprisingly, that, by combining an organic UV-A screening agent having a maximum absorption wavelength ( $\lambda_{\max}$ ) of less than 370 nm, such as 4-tert-butyl-4'-methoxydibenzoylmethane (Parsol® 1789;  $\lambda_{\max} = 358\ \text{nm}$ ), with certain zirconium, titanium and aluminum compounds, it is possible to obtain a material for which the absorption band is shifted and which exhibits a maximum absorption wavelength within the range from 370 to 400 nm, with an  $\epsilon$  value which is not significantly reduced.

A subject matter of the present invention is therefore a material capable of being obtained by the sol-gel route comprising at least one organic UV-A sunscreen agent with a  $\lambda_{\max}$  of less than 370 nm and at least one zirconium, titanium or aluminum compound, the material having a maximum absorption wavelength which is situated in the range from 370 to 400 nm.

The present invention also relates to a process for shifting the maximum absorption wavelength of an organic UV-A sunscreen agent with a  $\lambda_{\max}$  of less than 370 nm into the range from 370 to 400 nm.

A further subject matter of the present invention is cosmetic and/or dermatological compositions for the

photoprotection of the skin and/or keratinous substances comprising a material of the invention.

Other characteristics, aspects and advantages of the invention will become more clearly apparent on reading the description and examples which follow.

A subject matter of the present invention is a material capable of being obtained by the sol-gel route which exhibits a maximum absorption wavelength ( $\lambda_{\max}$ ) within the range from 370 to 400 nm and which comprises:

(a) at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides,

(b) at least one organic UV-A sunscreen agent, the maximum absorption wavelength of which is less than 370 nm,

(c) at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer,

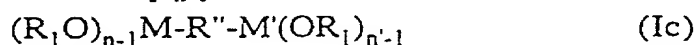
(d) at least one solvent, and

(e) an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation.

The term "organic UV-A sunscreen agent" is understood to mean any organic compound which absorbs UV radiation within the 320-400 nm wavelength range.

The metal alkoxides are chosen from the group composed of:

(1) metalloorganic compounds corresponding to one of the following formulae:



in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,  
n and n' denote the respective valencies of the metal atoms represented by M and M',

5 R<sub>1</sub> represents a saturated or unsaturated and linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, sulfur, oxygen or phosphorus atom, and more preferably a linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, alkyl group,

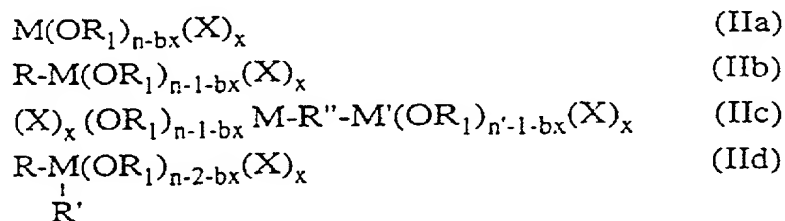
10 R and R' represent, independently of one another, a saturated or unsaturated and linear, branched or cyclic C<sub>1-30</sub>, preferably C<sub>2-20</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or  
15 branched alkyl group, a cycloalkyl group or an aryl group,

it being possible for said R and R' groups to be substituted by groups capable of reacting with the functionalized organic or silicone polymer, such as, for  
20 example, halogen atoms, the hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino or pyrrolo groups, groups comprising ethylenic unsaturation, such as the (meth)acrylic and vinyl groups,  
25 halogenated groups, such as perfluorinated groups, hydroxylated or carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate  
30 (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives, and the like, and it being possible for said R and R' groups to additionally comprise a cosmetically or dermatologically active group chosen, for example, from a colorant group, a  
35 photochromic group, a group for screening out UV radiation, a group for promoting adhesion to keratinous

substances (such as groups of amide, urethane, urea, hydroxyl, carboxyl, amino acid or polypeptide type), a group for facilitating the removal of makeup, a bactericidal group, a chelating group which can in particular complex polyvalent cations, a hydroxy acid, a neurosuppressant, a group for combating hair loss, an antioxidizing group, a group for combating free radicals or a vitamin-carrying group,

R'' represents a saturated or unsaturated and linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkylene group, a cycloalkylene group or an arylene group, it being possible for said R'' group to be substituted by groups capable of reacting with the organic or silicone polymer, such as those defined above, and it being possible for said R'' group additionally to comprise a cosmetically or dermatologically active group, such as those defined above;

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



in which:

M, M', n, n', R<sub>1</sub>, R, R' and R'' have the same meanings as those given for the above formulae (Ia) to (Id),

X represents a monodentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), such as, for example, those defined above, and which

can comprise a cosmetically or dermatologically active group, such as, for example, those defined above,

x represents the number of X ligands; and

b represents the number of bonding atoms of the X ligand.

5           The term "monodentate ligand" is understood to mean a group comprising a single atom which can bond to the central metal atom.

10           The term "chelating group" is understood to mean a polydentate ligand bonded to a single central metal atom by more than one doublet-donating atom.

15           Mention may be made, as examples of such monodentate or polydentate ligands (X), of sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids, preferably  
20            $\alpha$ - or  $\beta$ -hydroxylated amino acids, and their derivatives,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers),  
25           monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

30           Mention may in particular be made of diketones, such as 2,4-pentanedione, 2,4-hexafluoropentanedione or 2,2,6,6-tetramethyl-3,5-heptanedione; salicylic acid and  
35           its derivatives, such as 4- or 5-((meth)acrylamino)salicylic [sic] acid; lactic, succinic, acetic and citric acid; (meth)acrylic acid esters, such as acetoxyethyl methacrylate or methyl  $\alpha$ -hydroxy(meth)acrylate; ethyl acetoacetate, methyl acetoacetate and acetylacetone; EDTA; polyethers of low molecular mass, such as poly(ethylene glycol)s and poly(propylene glycol)s; polyethyleneimines; lysine and its derivatives, such as  $\epsilon$ -N-(meth)acryloyl-L-lysine; cysteine and its derivatives, such as N-acetylcysteine, carboxymethylcysteine, cystine or N,N'-diacetylcystine;

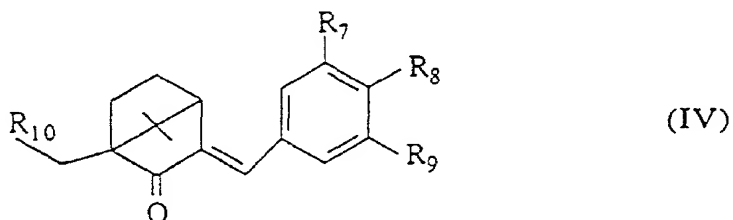
methionine; lactic acid esters or acetic acid esters; triethanolamine; lipoic acids; or dextrin or cyclodextrin.

5 Preference is very particularly given, among the metal alkoxides mentioned above, to tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

10 The organic UV-A sunscreen agent having a  $\lambda_{\text{max}}$  of less than 370 nm can be any appropriate organic compound having a maximum absorption wavelength of less than 370 nm.

Mention may be made, among organic UV-A sunscreen agents which can be used according to the invention, of:

- 15 (1) dibenzoylmethane derivatives;  
(2) screening agents active in the UV-A region of following formula (IV):

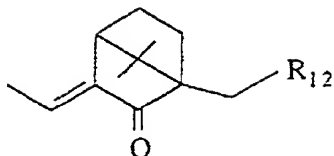


in which:

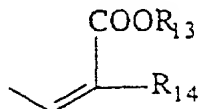
20  $R_7$  and  $R_9$ , which are identical or different, represent a hydrogen atom, a halogen atom, an OH group, a saturated or unsaturated and linear or branched  $C_1$ - $C_{10}$  alkyl group, a saturated or unsaturated and linear or branched  $C_1$ - $C_{10}$  alkoxy group or an  $HSO_3$  group;

$R_{10}$  represents a hydrogen atom or  $HSO_3$ ;

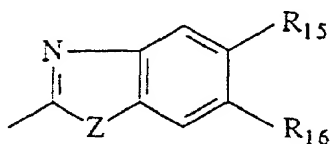
25  $R_8$  represents a hydroxyl group; an  $OR_{11}$  group where  $R_{11}$  represents a saturated or unsaturated and linear or branched  $C_1$ - $C_{10}$  alkyl group; or else a group of following structure:



in which  $R_{12}$  represents a hydrogen atom or  $HSO_3$ ;  
or else a group of following formula:



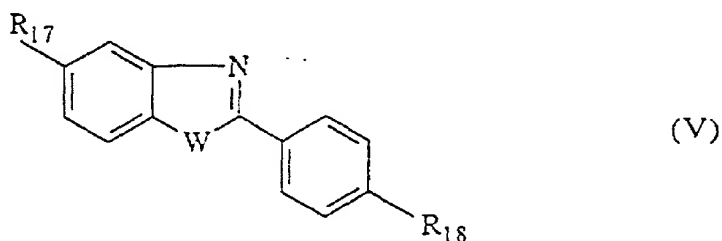
or else a a [sic] group of following formula:



in which:

5                   Z represents an oxygen atom or an -NH- group;

$R_{13}$ ,  $R_{14}$ ,  $R_{15}$  and  $R_{16}$ , which are identical or  
different, represent a hydrogen atom, a halogen atom, an  
OH group, a saturated or unsaturated and linear or  
branched  $C_1$ - $C_{10}$  alkyl group; a saturated or unsaturated and  
10 linear or branched  $C_1$ - $C_{10}$  alkoxy group; or an  $HSO_3$  group;  
(3) screening agents which are active in the UV-A region  
of the benzimidazole or benzoxazole type of following  
formula (V):



in which:

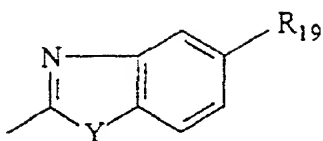
15                   W represents an oxygen atom or an -NH- group;

$R_{17}$  represents a hydrogen atom or  $HSO_3$ ;

$R_{18}$  represents a linear or branched alkoxy group  
comprising from 1 to 10 carbon atoms approximately or a



group of following formula:

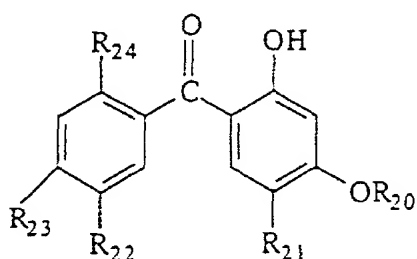


in which:

Y represents an oxygen atom or an -NH- group;

R<sub>19</sub> represents a hydrogen atom or HSO<sub>3</sub>;

- 5 (4) benzophenone derivatives, such as those of following formula (VI):



(VI)

in which

R<sub>20</sub> represents a hydrogen atom or a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl group;

- 10 R<sub>21</sub> and R<sub>22</sub>, which are identical or different, represent a hydrogen atom, a halogen atom, an OH group, a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl group; a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkoxy group or an HSO<sub>3</sub> group;

- 15 R<sub>23</sub> represents a hydrogen atom, OH, a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl group or a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkoxy group;

- 20 R<sub>24</sub> represents OH, a hydrogen atom or a saturated or unsaturated and linear or branched C<sub>1</sub>-C<sub>10</sub> alkyl group;

(5) silane derivatives or polyorganosiloxanes comprising benzophenone group(s), such as those disclosed in documents EP-A-0 389 377, FR-A-2 657 351 and EP-A-0 655 453;

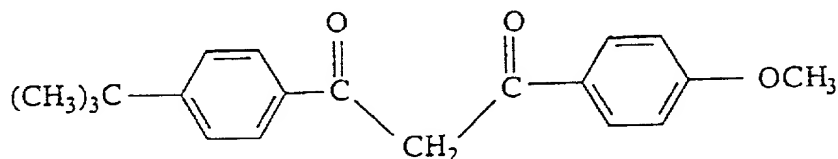
- 25 (6) anthranilates; and

(7) their mixtures.

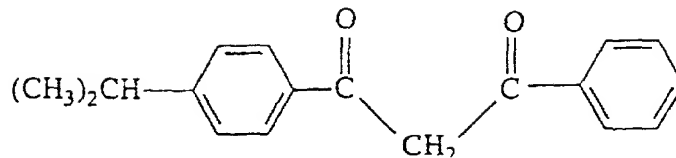
Mention may especially be made, among dibenzoylmethane derivatives which are particularly well suited in the context of the present invention, of, without implied limitation:

2-methyldibenzoylmethane,  
4-methyldibenzoylmethane,  
4-isopropyldibenzoylmethane,  
4-tert-butyldibenzoylmethane,  
2,4-dimethyldibenzoylmethane,  
2,5-dimethyldibenzoylmethane,  
4,4'-diisopropyldibenzoylmethane,  
4,4'-dimethoxydibenzoylmethane,  
4-tert-butyl-4'-methoxydibenzoylmethane,  
2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,  
2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,  
2,4-dimethyl-4'-methoxydibenzoylmethane,  
2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

Preference is in particular given, among the dibenzoylmethane derivatives mentioned above, to 4-tert-butyl-4'-methoxydibenzoylmethane, sold in particular under the trade name of "Parsol<sup>®</sup> 1789" by Hoffmann-Laroche, this screening agent corresponding to the following expanded formula:



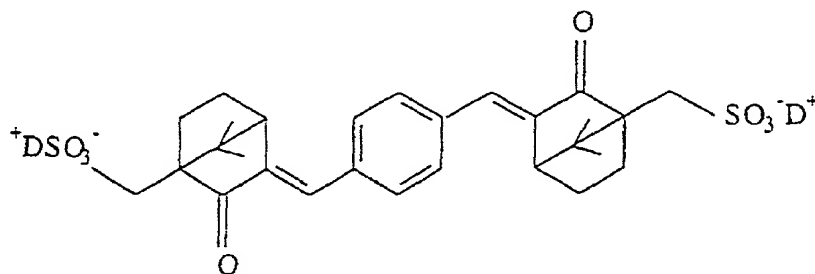
Another preferred dibenzoylmethane derivative according to the present invention is 4-isopropyldibenzoylmethane, sold under the name of "Eusolex<sup>®</sup> 8020" by Merck and corresponding to the following expanded formula:



The compounds of structures [sic] (IV) above are disclosed respectively in Patent US 4 585 597 and Patent Applications FR 2 236 515, 2 282 426, 2 645 148, 2 430 938 and 2 592 380.

5 A particularly preferred compound of formula (IV) is benzene-1,4-[di(3-methylidenecamphor-10-sulfonic acid)], such as the product sold under the name Mexoryl<sup>®</sup> SX by Chimex.

10 Benzene-1,4-[di(3-methylidenecamphor-10-sulfonic acid)] and its various salts (compound D), disclosed in particular in Patent Applications FR-A-2 528 420 and FR-A-2 639 347, are screening agents already known per se ("broad band" screening agents) capable in fact of absorbing ultraviolet rays with a wavelength ranging from 15 280 nm to 400 nm, with absorption maxima between 320 and 370 nm, in particular in the vicinity of 345 nm. These screening agents correspond to the following general formula:



20 in which D represents a hydrogen atom, an alkali metal or an  $\text{NH}(\text{R}_{25})_3^+$  group, in which the  $\text{R}_{25}$  groups, which can be identical or different, represent a hydrogen atom or a  $\text{C}_1$ - $\text{C}_4$  alkyl or hydroxyalkyl group, or an  $\text{M}^{n+}/n$  group,  $\text{M}^{n+}$  representing a polyvalent metal cation in which n is

equal to 2 or 3 or 4,  $M^{n+}$  preferably representing a metal cation chosen from  $Ca^{2+}$ ,  $Zn^{2+}$ ,  $Mg^{2+}$ ,  $Ba^{2+}$ ,  $Al^{3+}$  and  $Zr^{4+}$ . It is clearly understood that the compounds of formula (IV) above can give rise to the "cis-trans" isomer about one or more double bond(s) and that all the isomers come within the scope of the present invention.

Mention may be made, as examples of specific benzimidazole or benzoxazole compounds corresponding to the formula (V), of:

- 10           - benzene-1,4-di(benzimidazol-2-yl-5-sulfonic acid),
- benzene-1,4-di(benzoxazol-2-yl-5-sulfonic acid), and their partially or completely neutralized forms.

15           Mention may more particularly be made, among benzophenone derivatives of formula (VI), of those chosen from the group composed of:

- 2,4-dihydroxybenzophenone (benzophenone-1), such as the product sold under the name Uvinul<sup>®</sup> 400 by BASF;
- 20   - 2,2',4,4'-tetrahydroxybenzophenone (benzophenone-2), such as the product sold under the name Uvinul<sup>®</sup> D50 by BASF;
- 2-hydroxy-4-methoxybenzophenone, also known as oxybenzone (benzophenone-3), such as the product sold
- 25   under the name Uvinul<sup>®</sup> M40 by BASF;
- 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, also known as sulisobenzene (benzophenone-4), such as the product sold under the name Uvinul<sup>®</sup> MS40 by BASF; and its sodium sulfonate form (benzophenone-5);
- 30   - 2,2'-dihydroxy-4,4'-dimethoxybenzophenone (benzophenone-6), such as the product sold under the name Helisorb<sup>®</sup> 11 by Norquay;
- 5-chloro-2-hydroxybenzophenone (benzophenone-7);
- 2,2'-dihydroxy-4-methoxybenzophenone, also known as
- 35   dioxibenzone or benzophenone-8, such as the product sold under the name Spectrasorb<sup>®</sup> UV-24 by American Cyanamid;

- the disodium salt of 2,2'-dihydroxy-4,4'-dimethoxybenzophenone-5,5'-disulfonic diacid or benzophenone-9, such as the product sold under the name Uvinul<sup>®</sup> DS49 by BASF;
- 5 - 2-hydroxy-4-methoxy-4'-methylbenzophenone (benzophenone-10);
- benzophenone-11, such as the product sold under the name Uvinul<sup>®</sup> M493 by BASF;
- 2-hydroxy-4-(octyloxy)benzophenone (benzophenone-10  
12).

Mention may very particularly be made, among anthranilates which can be used according to the present invention, of menthyl anthranilate, such as the product sold under the name Neo Heliopan MA<sup>®</sup> by Haarman & Reimer.

15 The functionalized organic or silicone polymer of the material according to the invention can be a homopolymer or random, block and/or graft copolymer chosen from:

- (a) alkyloxazoline homopolymers and copolymers, such as  
20 poly(2-ethyl-2-oxazoline);
- (b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid  
25 and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins,  
30 styrene, substituted styrenes, such as hydroxystyrene, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, such as fluorovinyl ethers, and  
35 unsaturated organosilanes, organosiloxanes or organopolysiloxanes;

- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, such as hydroxystyrene, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, such as fluorovinyl ethers, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (f) polyethers, such as methylene oxide, ethylene oxide, propylene oxide or tetramethylene oxide homopolymers and copolymers;
- (g) aromatic and/or aliphatic polyesters, and polyesters obtained by ring opening, such as polycaprolactones, polylactides, polyglycolides and their copolymers;
- (h) homopolymers and copolymers of olefins or of cycloolefins, such as polyethylenes, ethylene/vinyl acetate, ethylene/ $\alpha$ -olefin, ethylene/cycloolefin or ethylene/(meth)acrylate copolymers, and propylene, butene, isobutene and norbornene homopolymers and copolymers;
- (i) polyamides, polyesteramides and polyetheramides;
- (j) optionally fluorinated polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers, such as the products sold by Ausimont under the name of "Fomblin<sup>®</sup>" (perfluoropolyether);
- (l) natural polymers and modified natural polymers, such as ether and/or ester derivatives of cellulose or of starch, polysaccharides, glycosaminoglucans and oligosaccharides, natural gums, such as hydroxyalkylated guar gums, such as those which are hydroxypropylated, hydroxypropylated guar gums

comprising carboxyl or quaternized functional groups, locust bean gum or xanthan gum, carrageenans, pectins, alginates, polypeptides or proteins, such as collagen, elastin, gelatin or keratin;

- (m) polyorganosiloxanes, such as polydimethylsiloxanes, polymethylphenylsiloxanes or polyphenylsiloxanes, or polyorganosiloxanes substituted on the chain or at the chain end by amino acid groups, polyoxyethylene chains, amino or polyamino groups, hydroxyl groups, carboxylic acid groups, alkyl chains, vinyl or acrylic grafts or blocks, or fluorinated or perfluorinated grafts or blocks;
- (n) polyorganophosphazenes;
- (o) polysilanes, polycarbosilanes or polysilazanes; and
- (p) mixtures of these polymers.

In a specific embodiment, the hydrocarbonaceous homopolymers and copolymers as mentioned above can possess polysiloxane chains as blocks and/or grafts.

The organic or silicone polymers can also comprise a cosmetically or dermatologically active group, such as those listed above.

In the case where organic or silicone polymers are not functionalized, they can be functionalized either by reaction within the actual composition, such as, for example, in the case of polyorganosiloxanes, or by prior reaction by conventional methods before the formation of the composition.

Mention may in particular be made, among preferred organic or silicone polymers according to the invention, of poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(vinyl alcohol [sic] and poly(vinylpyrrolidone). The most preferred are polydimethylsiloxane-diols.

When the material according to the invention comprises a precursor of the organic or silicone polymer, it is essentially one or more monomers capable of resulting in a functionalized organic or silicone polymer by polymerization of unsaturated double bonds or by polycondensation during application of the composition.

The polymerization can be initiated conventionally by a thermal route in the presence of conventional free radical initiators, by irradiation with UV radiation, by electron beams by the ionic route (cationic or anionic) or by any known polymerization technique.

Although this specific embodiment can be carried out according to the invention, it is nevertheless preferred, for practical reasons, to use a functionalized organic or silicone polymer which has already been formed.

The solvent used in the material of the present invention is preferably a linear or branched lower alcohol, better still ethanol.

The amounts of the various components of the material generally used are as follows, expressed with respect to the total weight of the material:

- from 0.1% by weight to 99% by weight, preferably from 0.5% by weight to 80% by weight and better still from 1% by weight to 70% by weight of metal alkoxide,
- from 0.1% by weight to 99% by weight, preferably from 0.5% by weight to 80% by weight and better still from 1% by weight to 70% by weight of functionalized organic or silicone polymer,
- from 0.1% by weight to 60% by weight, preferably from 0.1% by weight to 30% by weight and better still from 0.1% by weight to 20% by weight of sunscreen agent.

Another subject matter of the present invention relates to a process for shifting, into the range from 370 to 400 nm, the maximum absorption wavelength ( $\lambda_{\max}$ ) of



an organic UV-A screening agent having a  $\lambda_{\max}$  of less than 370 nm which consists in combining, with said screening agent, a sol comprising at least one functionalized organic polymer or one precursor of this polymer or at least one functionalized silicone polymer or one precursor of this polymer, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one solvent and an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation. All the components are as defined above.

According to a preferred embodiment of the process of the invention, the metal alkoxide is mixed with a polymer solution before the addition of the screening agent.

An additional subject matter of the present invention is a cosmetic and/or dermatological composition comprising, in a cosmetically and/or dermatologically acceptable vehicle, a material as defined above according to the present invention.

This cosmetic and/or dermatological composition comprises the material according to the invention in an effective amount ranging from 1% by weight to 99% by weight, preferably from 5% by weight to 60% by weight, with respect to the total weight of the composition. The material according to the invention is preferably dried and milled and added in the form of particles to the composition. The mean size of the particles which are obtained after drying and milling lies within the range from 0.1  $\mu\text{m}$  to 50  $\mu\text{m}$ , preferably from 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$  and better still from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

The cosmetic and/or dermatological compositions targeted by the present invention can, of course, comprise one or more additional sunscreen agents other than the organic UV-A sunscreen agents defined above, these additional sunscreen agents being water-soluble,

fat-soluble or insoluble in the cosmetic solvents commonly used. These additional screening agents can be chosen in particular from cinnamic acid derivatives, salicylic derivatives, camphor derivatives other than those corresponding to the formula (IV), triazine derivatives, such as those disclosed in Patent Applications US-4 367 390, EP 0 863 145, EP 0 517 104, EP 0 570 838, EP 0 796 851, EP 0 775 698, EP 0 878 469, EP 0 933 376 and EP 0 893 119,  $\beta,\beta'$ -diphenylacrylate derivatives, benzimidazole derivatives, bisbenzoazolyl derivatives, such as those disclosed in Patents EP 0 669 323 and US 2 463 264; methylenebis(hydroxyphenylbenzotriazol) derivatives, such as those disclosed in Applications US-5 237 071, US-5 166 355, GB-2 303 549, DE-19 726 184 and EP 0 893 119, p-aminobenzoic acid derivatives, and the screening hydrocarbonaceous and screening silicone polymers disclosed in Application WO-93/04665.

Mention may be made, as examples of additional active sunscreen agents, of:

- p-aminobenzoic acid,
- ethoxylated (25 mol) p-aminobenzoate,
- 2-ethylhexyl p-dimethylaminobenzoate,
- N-propoxylated ethyl p-aminobenzoate,
- glyceryl p-aminobenzoate,
- homomenthyl salicylate,
- 2-ethylhexyl salicylate,
- triethanolamine salicylate,
- 4-isopropylbenzyl salicylate,
- 2-ethylhexyl 4-methoxycinnamate,
- methyl diisopropylcinnamate,
- isoamyl 4-methoxycinnamate,
- diethanolamine 4-methoxycinnamate,
- 2-ethylhexyl 2-cyano-3,3-diphenyl acrylate,
- ethyl 2-cyano-3,3-diphenyl acrylate,
- 3-(4'-methylbenzylidene)-d,l-camphor,

- 3-benzylidene-d,l-camphor,
  - 2,4,6-tris[p-(2'-ethylhexyl-1'-oxycarbonyl)-anilino]-1,3,5-triazine,
  - 2-[(p-(tert-butylamido)anilino)-4,6-bis[(p-(2'-ethylhexyl-1'-oxycarbonyl)anilino)-1,3,5-triazine [sic],
  - 2,4-bis{[4-(2-ethylhexyloxy)-2-hydroxy]-phenyl}-6-(4-methoxyphenyl)-1,3,5-triazine [sic] (Tinosorb<sup>®</sup> S, Ciba-Geigy),
  - the polymer of N-(2- and 4-)[(2-oxoborn-3-yliden)methyl]benzyl]acrylamide [sic],
  - 1,4-bis(benzimidazolyl)phenylene-3,3',5,5'-tetrasulfonic [sic] acid and its soluble salts,
  - polyorganosiloxanes comprising a benzalmalonate functional group,
  - polyorganosiloxanes comprising a benzotriazole functional group, such as drometrizole trisiloxane,
  - 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl)phenol] in the dissolved form, such as the product sold under the trade name Mixxim<sup>®</sup> BB/100 by Fairmount Chemical, or else in the insoluble micronized form, such as the product sold under the trade name Tinosorb<sup>®</sup> M by Ciba-Geigy,
  - 2,2'-methylenebis[6-(2H-benzotriazol-2-yl)-4-(methyl)phenol] in the dissolved form, such as the product sold under the trade name Mixxim<sup>®</sup> BB/200 by Fairmount Chemical.
- 30       The cosmetic and/or dermatological compositions according to the invention can also comprise agents for the artificial tanning and/or browning of the skin (self-tanning agents), such as, for example, dihydroxyacetone (DHA).
- 35       The cosmetic and/or dermatological compositions according to the invention can also comprise pigments or

alternatively nanopigments (mean size of the primary particles: generally between 5 nm and 100 nm, preferably between 10 and 50 nm) formed of coated or uncoated metal oxides, such as, for example, nanopigments formed of titanium oxide (amorphous or crystalline titanium oxide in the rutile and/or anatase form), iron oxide, zinc oxide, zirconium oxide or cerium oxide, which are all photoprotective agents well known per se which act by physical blocking (reflection and/or scattering) of UV radiation. Conventional coating agents are, furthermore, alumina and/or aluminum stearate. Such nanopigments formed of coated or uncoated metal oxides are disclosed in particular in Patent Applications EP-A-0 518 772 and EP-A-0 518 773.

The cosmetic and/or dermatological compositions in accordance with the present invention can additionally comprise conventional cosmetic adjuvants chosen in particular from fatty substances, organic solvents, ionic or nonionic thickeners, softeners, antioxidants, agents for combating free radicals, opacifiers, stabilizers, emollients, silicones,  $\alpha$ -hydroxy acids, antifoaming agents, moisturizing agents, vitamins, fragrances, preservatives, surfactants, fillers, sequestering agents, polymers, propellants, basifying or acidifying agents, dyes or any other ingredient commonly used in the cosmetics and/or dermatological field, in particular for the manufacture of antisen compositions in the form of emulsions.

The fatty substances can be composed of an oil or a wax or their mixtures. The term "oil" is understood to mean a compound which is liquid at ambient temperature. The term "wax" is understood to mean a compound which is solid or substantially solid at ambient temperature and with a melting point generally of greater than 35°C.

Mention may be made, as oils, of mineral oils (liquid petrolatum); vegetable oils (sweet almond,

macadamia, blackcurrant seed or jojoba oil); synthetic oils, such as perhydrosqualene, fatty alcohols, acids or esters (such as the benzoate of C<sub>12</sub>-C<sub>15</sub> alcohols sold under the name "Finsolv TN" by Finetex, octyl palmitate, 5 isopropyl lanolate or triglycerides, including those of capric/caprillic acids), or ethoxylated or propoxylated fatty esters and ethers; silicone oils (cyclomethicone, preferably comprising 4 or 5 silicon atoms, or polydimethylsiloxane); fluorinated oils; or 10 polyalkylenes.

Mention may be made, as waxy compounds, of paraffin wax, carnauba wax, beeswax or hydrogenated castor oil.

Mention may be made, among organic solvents, of 15 lower alcohols and polyols.

The thickeners can be chosen in particular from crosslinked polyacrylic acids, modified or unmodified guar and cellulose gums, such as hydroxypropylated guar gum, methylhydroxyethylcellulose or hydroxypropyl- 20 methylcellulose, and silicone gums, such as, for example, a polydimethylsiloxane derivative.

The cosmetic and/or dermatological compositions according to the invention can be prepared according to techniques well known to a person skilled in the art, in 25 particular those intended for the preparation of emulsions of oil-in-water or water-in-oil type.

This cosmetic and/or dermatological composition can be provided in particular in the form of a simple or complex emulsion (O/W, W/O, O/W/O or W/O/W), such as a 30 cream or a milk, or in the form of a gel or of a cream gel, of a powder or of a solid stick and can optionally be packaged as an aerosol and be provided in the form of a foam or of a spray.

The cosmetic and/or dermatological compositions 35 according to the invention are preferably provided in the form of an oil-in-water emulsion.

When it is an emulsion, the aqueous phase of the latter can comprise a nonionic vesicular dispersion prepared according to known processes (Bangham, Standish and Watkins, J. Mol. Biol., 13, 238 (1965), FR 2 315 991 and FR 2 416 008).

The cosmetic and/or dermatological composition according to the invention is used as composition for protecting the skin or keratinous substances against ultraviolet rays, as antisun composition or as makeup product.

When the cosmetic composition according to the invention is used for protecting the hair, it can be provided in the form of a shampoo, lotion, gel, emulsion or nonionic vesicular dispersion and can constitute, for example, a rinse-out composition, to be applied before or after shampooing, before or after dyeing or bleaching, or before, during or after perming or hair straightening, a styling or treating lotion or gel, a lotion or a gel for blow drying or hairsetting, or a composition for perming or straightening or for dyeing or bleaching the hair.

By way of indication, for antisun formulations in accordance with the invention which exhibit a vehicle of oil-in-water emulsion type, the aqueous phase (comprising in particular hydrophilic screening agents) generally represents from 50 to 95% by weight, preferably from 70 to 90% by weight, with respect to the entire formulation, the oily phase (comprising in particular lipophilic screening agents) from 5 to 50% by weight, preferably from 10 to 30% by weight, with respect to the entire formulation and the (co)emulsifier(s) from 0.5 to 20% by weight, preferably from 2 to 10% by weight, with respect to the entire formulation.

The examples are given by way of illustration of the present invention and are not understood in any way to be limiting.

Example 1

A material according to the invention is prepared from:

	Tetra-n-propyl zirconate	9.36 g
5	Absolute ethanol	2.83 g
	Polydimethylsiloxane-diol (PDMS-diol)	6.24 g
	Parsol <sup>®</sup> 1789	0.08 g
	Water	0.02 g

10 the tetra-n-propyl zirconate originating from Fluka, the Parsol<sup>®</sup> 1789 (4-tert-butyl-4'-methoxydibenzoylmethane) being sold by Hoffmann-Laroche and the PDMS-diol exhibiting a weight-average molar mass of 550 (ABCR, reference DMS-S12).

15 The PDMS-diol is diluted in ethanol. The tetra-n-propyl zirconate is subsequently added and the mixture is stirred for 5 minutes. The Parsol<sup>®</sup> 1789 is subsequently added with stirring. The novel material is ready for use.

20 Application and evaluation

The novel material is deposited on a glass sheet (microscope slide). A film is formed on the sheet after evaporation of the volatile components of the mixture. The drying time of the film is fast, that is to say  
25 between 1 and 3 minutes.

The absorption band of the novel material is evaluated by UV visible absorption spectrometry. The  $\lambda_{\max}$  value has shifted to 378 nm with respect to the  $\lambda_{\max}$  of 358 nm of Parsol<sup>®</sup> 1789 before the preparation of the  
30 material. The effectiveness of the novel material is not significantly reduced. This novel material is able to form a film, is entirely persistent toward water and ethanol and is not released under these conditions and in polar and nonpolar cosmetic oils.

35

Example 2

A material according to the invention is prepared from:

	Titanium tetraisopropoxide	2.27 g
5	Absolute ethanol	0.50 g
	Polydimethylsiloxane-diol (PDMS-diol)	0.40 g
	Parsol <sup>®</sup> 1789	1.10 g
	Tetrahydrofuran (THF)	2.25 g

10 the titanium tetraisopropoxide originating from Fluka, the Parsol<sup>®</sup> 1789 (4-tert-butyl-4'-methoxydibenzoylmethane) being sold by Hoffmann-Laroche, the PDMS-diol exhibiting a weight-average molar mass of 550 (ABCR, reference DMS-S12) and the tetrahydrofuran originating from Fluka.

15 The titanium tetraisopropoxide is diluted in ethanol. The Parsol<sup>®</sup> 1789, dissolved in the THF, is subsequently added to the solution with stirring over 20 minutes and then the PDMS-diol is added. The mixture is left to stir at ambient temperature for 60 minutes. The  
20 novel material is then ready for use.

Application and evaluation

The application and evaluation are carried out in the same way as in Example 1. The  $\lambda_{\max}$  value was shifted  
25 to 385 nm with respect to the  $\lambda_{\max}$  of 358 nm of Parsol<sup>®</sup> 1789 before the preparation of the material. The effectiveness of the novel material was not significantly reduced. This novel material is able to form a film, is entirely persistent toward water and ethanol and is not  
30 released under these conditions and in polar and nonpolar cosmetic oils.

Example 3

35 A material according to the invention is prepared from:



	Aluminum tri-sec-butoxide at 75% in sec-	
	butanol	0.36 g
	Polydimethylsiloxane-diol (PDMS-diol)	0.44 g
	Parsol <sup>®</sup> 1789	0.23 g
5	Tetrahydrofuran (THF)	2.25 g

the aluminum tri-sec-butoxide originating from ABCR, the  
Parsol<sup>®</sup> 1789 (4-tert-butyl-4'-methoxydibenzoylmethane)  
being sold by Hoffmann-Laroche, the PDMS-diol exhibiting  
10 a weight-average molar mass of 550 (ABCR, reference DMS-  
S12) and the tetrahydrofuran originating from Fluka.

The Parsol<sup>®</sup> 1789, dissolved in the THF, is added,  
with stirring over 20 minutes, to the solution of  
aluminum tri-sec-butoxide in sec-butanol and then the  
15 PDMS-diol is added. The mixture is left to stir at  
ambient temperature for 60 minutes. The novel material is  
then ready for use.

#### Application and evaluation

20 The application and evaluation are carried out in  
the same way as in Example 1. The  $\lambda_{\text{max}}$  value was shifted  
to 370 nm with respect to the  $\lambda_{\text{max}}$  of 358 nm of Parsol<sup>®</sup>  
1789 before the preparation of the material. The  
effectiveness of the novel material was not significantly  
25 reduced. This novel material is able to form a film, is  
entirely persistent toward water and ethanol and is not  
released under these conditions and in polar and nonpolar  
cosmetic oils.

# CLAIMS

1. Material capable of being obtained by the sol-gel route comprising:

5 (a) at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides,

(b) at least one organic UV-A sunscreen agent having a maximum absorption wavelength of less than 370 nm,

10 (c) at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer,

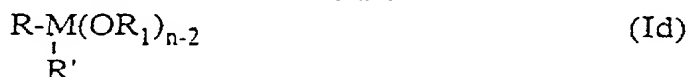
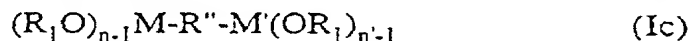
(d) at least one solvent, and

15 (e) an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation,

said material having a maximum absorption wavelength ( $\lambda_{\max}$ ) which is situated in the range from 370 to 400 nm.

20 2. Material according to Claim 1, characterized in that the metal alkoxide is chosen from the group composed of:

(1) metalloorganic compounds corresponding to one of the following formulae:



25 in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,

n and n' denote the respective valencies of the metal atoms represented by M and M',

30 R<sub>1</sub> represents a saturated or unsaturated and linear or

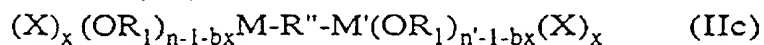
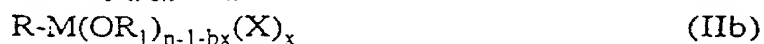
branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, sulfur, oxygen or phosphorus atom, and more preferably a linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, alkyl group,

5 R and R' represent, independently of one another, a saturated or unsaturated and linear, branched or cyclic C<sub>1-30</sub>, preferably C<sub>2-20</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or  
10 branched alkyl group, a cycloalkyl group or an aryl group,

it being possible for said R and R' groups to be substituted by groups capable of reacting with the organic or silicone polymer and it being possible for  
15 said R and R' groups to additionally comprise a cosmetically or dermatologically active group,

R'' represents a saturated or unsaturated and linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen,  
20 phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkylene group, a cycloalkylene group or an arylene group, it being possible for said R'' group to be substituted by groups capable of reacting with the organic or silicone polymer and it being  
25 possible for said R'' group additionally to comprise a cosmetically or dermatologically active group;

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



in which:

30 M, M', n, n', R<sub>1</sub>, R, R' and R'' have the same meanings as

those given for the above formulae (Ia) to (Id),

X represents a monodentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), and which can comprise a cosmetically or dermatologically active group,

x represents the number of X ligands; and

b represents the number of bonding atoms of the X ligand.

3. Material according to Claim 2, characterized in that said group capable of reacting with the functionalized organic polymer or the functionalized silicone polymer (c) carried by the R, R' or R'' group and/or by the X ligand can be chosen from halogen atoms, the hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino or pyrrolo groups, groups comprising ethylenic unsaturation, such as the (meth)acrylic and vinyl groups, halogenated groups, such as perfluorinated groups, hydroxylated or carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives.

4. Material according to Claim 2 or 3, characterized in that the monodentate or polydentate ligand X is chosen from sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids, preferably  $\alpha$ - or  $\beta$ -hydroxylated amino acids, and their derivatives,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers),

monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

5. Material according to any one of the preceding claims, characterized in that the metal alkoxide is  
5 chosen from tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

6. Material according to any one of the preceding claims, characterized in that the metal alkoxide is  
10 present in an amount ranging from 0.1% by weight to 99% by weight, preferably from 0.5% to 80% by weight, with respect to the total weight of the material.

7. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen  
15 agent is chosen from:

- dibenzoylmethane derivatives,
- camphor derivatives,
- benzimidazole derivatives,
- benzoxazole derivatives,
- 20 - benzophenone derivatives,
- silane or polyorganosiloxane derivatives comprising benzophenone group(s),
- anthranilates, and
- their mixtures.

8. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen  
25 agent is chosen from:

- 2-methyldibenzoylmethane,
- 4-methyldibenzoylmethane,
- 30 - 4-isopropyldibenzoylmethane,
- 4-tert-butyldibenzoylmethane,
- 2,4-dimethyldibenzoylmethane,
- 2,5-dimethyldibenzoylmethane,
- 4,4'-diisopropyldibenzoylmethane,
- 35 - 4,4'-dimethoxydibenzoylmethane,
- 4-tert-butyl-4'-methoxydibenzoylmethane,

- 2-methyl-5-isopropyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-tert-butyl-4'-methoxydibenzoylmethane,
- 2,4-dimethyl-4'-methoxydibenzoylmethane,
- 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

9. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen agent is 4-tert-butyl-4'-methoxydibenzoylmethane.

10. Material according to any one of the preceding claims, characterized in that the organic UV-A sunscreen agent is present in an amount ranging from 0.1% by weight to 60% by weight, preferably from 0.1% to 30% by weight, with respect to the total weight of the material.

11. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is a homopolymer or random, block and/or graft copolymer chosen from:

- (a) alkyloxazoline homopolymers and copolymers;
- (b) homopolymers and copolymers of (meth)acrylic acid, of crotonic acid, of maleic acid, of itaconic acid, of styrenesulfonic acid, of 2-(acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl

esters or amides and their copolymers with comonomers chosen from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;

(f) polyethers;

10 (g) polyesters;

(h) homopolymers and copolymers of olefins or of cycloolefins;

(i) polyamides and polyesteramides;

15 (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;

(k) fluoropolymers;

(l) natural polymers and modified natural polymers;

(m) polyorganosiloxanes;

20 (n) polyorganophosphazenes;

(o) polysilanes, polycarbosilanes or polysilazanes; and

(p) mixtures of these polymers.

12. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is chosen from poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s, poly(amy1 [sic] alcohol) and poly(vinylpyrrolidone).

30 13. Material according to Claim 12, characterized in that the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.

14. Material according to any one of the preceding claims, characterized in that the functionalized organic or silicone polymer is present in an amount ranging from 35 0.1% by weight to 99% by weight, preferably from 0.5% to

80% by weight, with respect to the total weight of the material.

15. Material according to any one of the preceding claims, characterized in that the solvent is an alcohol.

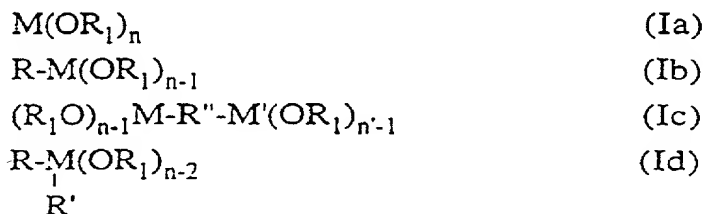
16. Material according to Claim 15, characterized in that the alcohol is a linear or branched lower alcohol.

17. Material according to Claim 16, characterized in that the alcohol is ethanol.

18. Process for shifting the maximum absorption wavelength ( $\lambda_{\max}$ ) of an organic UV-A sunscreen agent having a  $\lambda_{\max}$  of less than 370 nm into the range from 370 to 400 nm, characterized in that it comprises the combination of this screening agent with a sol comprising at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one solvent and an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation.

19. Process according to Claim 18, characterized in that the metal alkoxide is chosen from the group composed of:

(1) metalloorganic compounds corresponding to one of the following formulae:



in which:

M and M' represent, independently of one another, a zirconium, titanium or aluminum atom,

n and n' denote the respective valencies of the metal



atoms represented by M and M',

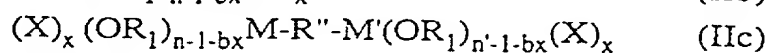
R<sub>1</sub> represents a saturated or unsaturated and linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, sulfur, oxygen or phosphorus atom, and more preferably a linear or branched C<sub>1-30</sub>, preferably C<sub>1-6</sub>, alkyl group,

R and R' represent, independently of one another, a saturated or unsaturated and linear, branched or cyclic C<sub>1-30</sub>, preferably C<sub>2-20</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkyl group, a cycloalkyl group or an aryl group,

it being possible for said R and R' groups to be substituted by groups capable of reacting with the organic or silicone polymer and it being possible for said R and R' groups to additionally comprise a cosmetically or dermatologically active group,

R'' represents a saturated or unsaturated and linear, branched or cyclic divalent C<sub>1-30</sub>, hydrocarbonaceous group optionally comprising a heteroatom, such as a nitrogen, phosphorus, sulfur or oxygen atom, such as, for example, a linear or branched alkylene group, a cycloalkylene group or an arylene group, it being possible for said R'' group to be substituted by groups capable of reacting with the organic or silicone polymer and it being possible for said R'' group additionally to comprise a cosmetically or dermatologically active group;

(2) complexed or chelated metalloorganic compounds corresponding to one of the following formulae:



in which:

M, M', n, n', R<sub>1</sub>, R, R' and R'' have the same meanings as those given for the above formulae (Ia) to (Id),

X represents a monodentate ligand or a chelating group comprising a nitrogen atom, a phosphorus atom, a sulfur atom or an oxygen atom which can be covalently bonded to a group capable of reacting with said functionalized organic polymer or said functionalized silicone polymer (c), and which can comprise a cosmetically or dermatologically active group,

x represents the number of X ligands; and

b represents the number of bonding atoms of the X ligand.

20. Process according to Claim 19, characterized in that said group capable of reacting with the functionalized organic polymer or the functionalized silicone polymer (c) carried by the R, R' or R'' group and/or by the X ligand can be chosen from halogen atoms, the hydroxyl, acyl, carboxyl, ester, thiol, alkylthioalkyl, epoxy, isocyanate, thiocyanate, ureido, thioureido, urethane, imidazolo, morpholino or pyrrolo groups, groups comprising ethylenic unsaturation, such as the (meth)acrylic and vinyl groups, halogenated groups, such as perfluorinated groups, hydroxylated or carboxylated groups, phosphonic, phosphonate, phosphate, pyrophosphate, phosphonium, sulfonate, amine, quaternary ammonium, amide, amino acid and polypeptide groups, the acetic acid, acetoacetate (ACAC) or ethyl acetoacetate group, or a group deriving from EDTA and its derivatives.

21. Process according to Claim 19 or 20, characterized in that the monodentate or polydentate ligand X is chosen from sulfuric acids, sulfonic acids, phosphonic acids, phosphoric acids, carboxylic acids, ketones,  $\beta$ -diketones, esters,  $\beta$ -ketoesters, amines,  $\beta$ -ketoamines, amino acids, preferably  $\alpha$ - or  $\beta$ -hydroxylated amino acids, and their derivatives,  $\alpha$ - or  $\beta$ -hydroxy acids, ethers and polyethers, imines, optionally

hydroxylated amides, azo compounds, thiols, ureas, thioether sulfoxides, thioether sulfones, optionally cyclic thioethers, di(thioethers), monoalcohols or polyols, dextrin and its derivatives, or thiazolidines.

5 22. Process according to any one of Claims 18 to 21, characterized in that the metal alkoxide is chosen from tetra-n-propyl zirconate, tetraisopropyl zirconate, titanium tetraisopropoxide and aluminum tri-sec-butoxide.

10 23. Process according to any one of Claims 18 to 22, characterized in that the organic UV-A sunscreen agent is chosen from:

- dibenzoylmethane derivatives,
- camphor derivatives,
- benzimidazole derivatives,
- 15 - benzoxazole derivatives,
- benzophenone derivatives,
- silane or polyorganosiloxane derivatives comprising benzophenone group(s),
- anthranilates, and
- 20 - their mixtures.

24. Process according to any one of Claims 18 to 23, characterized in that the organic UV-A sunscreen agent is chosen from:

- 2-methyldibenzoylmethane,
- 25 - 4-methyldibenzoylmethane,
- 4-isopropyldibenzoylmethane,
- 4-tert-butyldibenzoylmethane,
- 2,4-dimethyldibenzoylmethane,
- 2,5-dimethyldibenzoylmethane,
- 30 - 4,4'-diisopropyldibenzoylmethane,
- 4,4'-dimethoxydibenzoylmethane,
- 4-tert-butyl-4'-methoxydibenzoylmethane,
- 2-methyl-5-isopropyl-4'-methoxydibenzoyl-methane,
- 35 - 2-methyl-5-tert-butyl-4'-methoxydibenzoyl-methane,

- 2,4-dimethyl-4'-methoxydibenzoylmethane,
- 2,6-dimethyl-4-tert-butyl-4'-methoxydibenzoylmethane.

25. Process according to any one of Claims 18 to 24,  
5 characterized in that the organic UV-A sunscreen agent is 4-tert-butyl-4'-methoxydibenzoylmethane.

26. Process according to any one of Claims 18 to 25,  
characterized in that the functionalized organic or  
silicone polymer is a homopolymer or random, block and/or  
10 graft copolymer chosen from:

- (a) alkyloxazoline homopolymers and copolymers;
- (b) homopolymers and copolymers of (meth)acrylic acid,  
of crotonic acid, of maleic acid, of itaconic acid,  
of styrenesulfonic acid, of 2-  
15 (acrylamido)methylpropanesulfonic acid, of 2-sulfoethyl methacrylate, of vinylsulfonic acid and/or of vinylphosphonic acid;
- (c) homopolymers of acrylic or methacrylic esters or amides and their copolymers with comonomers chosen  
20 from unsaturated carboxylic acids, sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds and unsaturated organosilanes, organosiloxanes or organopolysiloxanes;
- (d) vinyl alcohol homopolymers and copolymers;
- (e) homopolymers of vinyl and/or allyl and/or methallyl  
esters or amides and their copolymers with  
comonomers chosen from unsaturated carboxylic acids,  
30 sulfonic acids, phosphonic acids, vinyl esters and ethers, olefins, styrene, substituted styrenes, fluoro- and perfluoroolefins, perfluoroalkyl (meth)acrylates, fluorovinyl compounds, and unsaturated organosilanes, organosiloxanes or  
35 organopolysiloxanes;
- (f) polyethers;

- (g) polyesters;
- (h) homopolymers and copolymers of olefins or of cycloolefins;
- (i) polyamides and polyesteramides;
- 5 (j) polyurethanes and polyureas which can comprise polyether, polyester and/or polyorganosiloxane blocks;
- (k) fluoropolymers;
- (l) natural polymers and modified natural polymers;
- 10 (m) polyorganosiloxanes;
- (n) polyorganophosphazenes;
- (o) polysilanes, polycarbosilanes or polysilazanes; and
- (p) mixtures of these polymers.

27. Process according to any one of Claims 18 to 26,  
15 characterized in that the functionalized organic or silicone polymer is chosen from poly(2-ethyl-2-oxazoline), a terpolymer of vinyl acetate, of vinyl 4-tert-butylbenzoate and of crotonic acid (62/25/10), polydimethylsiloxane-diols, poly(ethylene glycol)s,  
20 poly(amyl [sic] alcohol) and poly(vinylpyrrolidone).

28. Process according to Claim 28, characterized in that the functionalized organic or silicone polymer is a polydimethylsiloxane-diol.

29. Process according to any one of Claims 18 to 28,  
25 characterized in that the solvent is a linear or branched lower alcohol.

30. Process according to Claim 29, characterized in that the alcohol is ethanol.

31. Process according to any one of Claims 18 to 30,  
30 characterized in that the metal alkoxide is mixed with a solution of functionalized organic or silicone polymer before the addition of the screening agent.

32. Cosmetic and/or dermatological composition, characterized in that it comprises, in a cosmetically  
35 and/or dermatologically acceptable vehicle, an effective amount of the material according to any one of Claims 1

to 17.

33. Cosmetic and/or dermatological composition according to Claim 32, characterized in that the material is in the form of particles obtained by drying and milling.

34. Cosmetic and/or dermatological composition according to Claim 32 or 33, characterized in that the effective amount of the material according to any one of Claims 1 to 17 lies within the range from 1% by weight to 99% by weight with respect to the total weight of the cosmetic and/or dermatological composition.

35. Cosmetic and/or dermatological composition according to any one of Claims 32 to 34, characterized in that the effective amount of the material according to any one of Claims 1 to 17 lies within the range preferably from 5 to 60% by weight with respect to the total weight of the cosmetic and/or dermatological composition.

36. Cosmetic and/or dermatological composition according to any one of Claims 32 to 35, characterized in that the mean size of the particles obtained by drying and milling the material according to any one of Claims 1 to 17 lies within the range from 0.1  $\mu\text{m}$  to 20  $\mu\text{m}$ .

37. Cosmetic and/or dermatological composition according to Claim 36, characterized in that the mean size of the particles obtained by drying and milling the material according to any one of the Claims 1 to 17 lies within the range from 0.1  $\mu\text{m}$  to 10  $\mu\text{m}$ .

38. Cosmetic and/or dermatological composition according to any one of Claims 32 to 37, characterized in that an additive chosen from sunscreen agents other than organic UV-A sunscreen agents, agents for the artificial tanning and/or browning of the skin, pigments, fatty substances, organic solvents, thickeners, softeners or antioxidants can additionally be added.

## ABSTRACT

### MATERIAL COMPRISING AN ORGANIC UV-A SCREENING AGENT AND PROCESS FOR SHIFTING THE MAXIMUM ABSORPTION WAVELENGTH

The present invention generally relates to a material capable of being obtained by the sol-gel route exhibiting a maximum absorption wavelength ( $\lambda_{\text{max}}$ ) within the range from 370 to 400 nm, said material comprising at least one organic UV-A sunscreen agent having a  $\lambda_{\text{max}}$  of less than 370 nm, at least one metal alkoxide chosen from zirconium, titanium and aluminum alkoxides, at least one functionalized organic polymer or one precursor of such a polymer, or at least one functionalized silicone polymer or one precursor of such a polymer, at least one solvent and an amount of water sufficient for the partial and/or complete hydrolysis of the metal alkoxide and its condensation. The present invention also relates to a process for shifting, into the range from 370 to 400 nm, the maximum absorption wavelength of an organic UV-A sunscreen agent having a  $\lambda_{\text{max}}$  of less than 370 nm and to a cosmetic and/or dermatological composition for the photoprotection of the skin and/or keratinous substances comprising a material of the invention.

**DECLARATION AND POWER OF ATTORNEY  
UNITED STATES PATENT APPLICATION**

Attorneys' Docket

As a below named inventor, I declare that:

My residence, post office address and citizenship are stated below to my name.

I believe I am the original, first and sole inventor (if only one name is listed below), or an original first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which patent is sought on the invention entitled:

**MATERIAL COMPRISING AN ORGANIC UV-A FILTER AND METHOD FOR DISPLACING THE MAXIMUM ABSORPTION WAVELENGTH.**

(check one) ( ) is attached hereto

( ) was filed as U.S. Application No. \_\_\_\_\_ on \_\_\_\_\_

and (if applicable) was amended on \_\_\_\_\_

(X) was filed as PCT International Application No. **PCT/FR00/02687** on **28 September 2000**

and (if applicable) was amended under PCT Article 19 on \_\_\_\_\_

(I authorize any attorney appointed below to insert information in the preceding blanks.)

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, § 119(a)-(d) or §365(d) of any foreign and PCT application(s) for patent or inventor's certificate, or §365(a) of any PCT international application which designated at least one country other than the United States of America listed in this Declaration.

I have also identified below any foreign application for patent or inventor's certificate or PCT international application having a filing date before that of the application(s) on which priority is claimed.

Foreign/PCT Appln. N°	Country	Filing Date	Priority Claimed (Yes / No)
99/12321	FRANCE	1 October 1999	Yes

I hereby claim the benefit under Title 35, United States Code §120 or §365(c) of any United States application and PCT international application designating the United States listed in this Declaration and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

U.S. Application N°	Filing Date	Status (patented/pending/abandoned)

I hereby claim benefits under Title 35 United States Code §119(e) of any U.S. provisional application(s) listed below:

U.S. Provisional Appln. N°	Filing Date

And I hereby appoint Pillsbury Winthrop LLP, Intellectual Property Group, 1100 New York Avenue, N.W., Ninth Floor, East Tower, Washington, D.C. 20005-3918, telephone number (202) 861-3000 (to whom all communications are to be directed), and the below-named persons (of the same address) individually and collectively my attorneys to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith and with the resulting patent, and I hereby authorize them to delete names/numbers below of persons no longer with their firm and to act and rely on instructions from and communicate directly with the person/assignee/attorney/firm/ organization who/which first sends/sent this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instruct the above Firm and/or a below attorney in writing to the contrary.

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I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code; and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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